

# Enhancing nitrate reduction to ammonia by synergistic and interface coupling effects of binary metal sites

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## ABSTRACT

Electrochemical nitrate reduction to ammonia (NRA) provides a sustainable and energy-efficient technical solution. Herein, we reported a synergistic bimetallic oxides  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  with heterointerfaces for efficient NRA. The interfacial charge transfer at the heterointerfaces between  $\text{Fe}_3\text{O}_4$  and  $\text{SnO}_2$  improves the adsorption and activation of nitrate and intermediates, and strongly inhibits the production of by-products ( $\text{NO}_2^-$ ) and the occurrence of HER. Experimental and theoretical results verify that the Fe sites activate  $\text{NO}_3^-$ , while the Sn sites dissociate  $\text{H}_2\text{O}$  molecules to provide necessary  $^*\text{H}$  for the Fe sites to reduce  $\text{NO}_3^-$ . Benefiting from the interfacial engineering and synergistic effect of Fe and Sn,  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  exhibits excellent NRA performance ( $\text{NH}_3$  Faradaic efficiency: 98.78%,  $\text{NH}_3$  yield:  $0.2584 \text{ mmol h}^{-1} \text{ cm}^{-2}$ ,  $\text{NH}_3$  selectivity: 98.85%, and  $\text{NO}_3^-$  conversion: 90.19%), which is significantly superior to  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$ . This work provides a powerful approach for constructing synergistic heterojunction and contribute a promising strategy for designing efficient electrocatalysts.

## 1. Introduction

Ammonia ( $\text{NH}_3$ ) is one of the most produced chemicals in the world, accounting for 5% of the market value of chemical products, and 80% of ammonia is used for producing agricultural fertilizers. Besides,  $\text{NH}_3$  is a feedstock for medicine, refrigerant, and fabrics. Currently, thermochemical methods for  $\text{NH}_3$  synthesis (the Haber-Bosch process) rely on high temperature and high pressure to drive chemical reactions. Consumption of natural gas and emissions of  $\text{CO}_2$  lead to serious energy and environmental problems [1–3]. Electrochemical reduction of nitrogen ( $\text{N}_2$ ) to synthesize  $\text{NH}_3$  (NRR) is a promising alternative to the energy intensive Hubble-Bosch process. However, NRR typically results in relatively low  $\text{NH}_3$  yield and  $\text{NH}_3$  Faraday efficiency (FE) due to its extremely low  $\text{N}_2$  solubility, ultra-stable  $\text{N}\equiv\text{N}$  bond, and severe competitive hydrogen evolution reaction (HER) [4–6].

The electrochemical nitrate reduction to ammonia (NRA),  $\text{NO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$ , is another candidate pathway for ammonia synthesis [1,7,8]. Nitrate is one of the main environmental pollutants,

and widely exists in industrial wastewater and domestic sewage [9]. NRA not only achieves the production of ammonia, but also the environmental remediation. Due to the significantly lower dissociation energy of the N-O bond ( $204 \text{ kJ mol}^{-1}$ ) of the adsorbed reactant  $\text{NO}_3^-$  compared to the  $\text{N}\equiv\text{N}$  bond ( $941 \text{ kJ mol}^{-1}$ ) of  $\text{N}_2$ , NRA is more prone to occur than NRR [10–12]. Moreover,  $\text{NO}_3^-$  can be adsorbed to the surface of catalysts more easily than  $\text{N}_2$  under ambient conditions. However, the difficulty of charge transfer to the  $\pi$ -orbital of nitrate results in sluggish reaction kinetics in the NRA process [13,14]. Therefore, there is an urgent need to develop powerful catalysts to promote the conversion of  $\text{NO}_3^-$  to  $\text{NH}_3$  while inhibiting by-products and competing HER [15,16].

NRA involves not only nitrate adsorption but also a hydrogenation process that is heavily dependent on water splitting [17–21].  $^*\text{H}$  produced by dissociating water is captured by the intermediates of  $\text{NO}_3^-$  to  $\text{NH}_3$ , facilitating the hydrogenation process of  $\text{NO}_3^-$  reduction. With the advantages of non-toxicity, wide availability, and low cost, iron-based catalysts have become a promising material for electrochemical NRA in recent years. The unfilled 3d orbital of iron can easily pair with the

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extranuclear electrons of O in the N-O bond of nitrate, thus favoring the adsorption of  $\text{NO}_3^-$  [22]. However, the  $\text{Fe}_3\text{O}_4$  surface lacks inherent active sites for the adsorption of  $^*\text{H}$  [23,24], which is unfavorable for the hydrogenation of nitrate reduction. It has been shown that  $\text{SnO}_2$  can play a role adsorbing  $^*\text{OH}$  during water splitting, which promotes the formation of  $^*\text{H}$  [25,26]. The moderate adsorption strength of H on catalyst surface facilitates ammonia formation and also inhibits H-H dimerization [18,27]. Interestingly, the heterointerfaces of catalyst can integrate the functions of multiple components and modulate the electronic structure of each component to induce charge redistribution [28]. It is reported that the interfacial engineering can effectively boost the NRA efficiency by optimizing the adsorption strength of nitrate, increasing electron transfer rate and exposing more active sites [29–32]. Therefore, designing and synthesizing iron-based/ $\text{SnO}_2$  catalysts based on interfacial engineering to achieve division of labor among various components and synergistically improve the performance of NRA is a promising strategy.

Herein,  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  with heterointerfaces was synthesized by a combination of hydrothermal and calcination methods.  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  obtains an outstanding electrocatalytic NRA performance with FE of 98.78%,  $\text{NH}_3$  yield of  $0.2548 \text{ mmol h}^{-1} \text{ cm}^{-2}$ ,  $\text{NH}_3$  selectivity of 98.85% and  $\text{NO}_3^-$  conversion of 90.19% at  $-0.49 \text{ V}$ , which are significantly better than that of the contrast samples  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$ . Experimental and theoretical results show that charge redistribution at heterointerfaces modulates the electronic structures of  $\text{Fe}_3\text{O}_4$  and  $\text{SnO}_2$  and thus enhances the adsorption of  $\text{NO}_3^-$  and intermediates. Of particular interest is that during catalytic processes, the Fe atom is acted as the active site for adsorbing nitrate, while Sn is the active site for dissociating water molecules to generate H. This synergistic effect of Fe and Sn sites on the heterointerfaces promotes the adsorption and activation of  $\text{NO}_3^-$  and inhibits the occurrence of HER, resulting in the excellent NRA performance of the  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  catalyst.

## 2. Experimental section

### 2.1. Synthesis of $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ with heterointerfaces

The  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  catalyst with heterointerfaces was fabricated using a combination of hydrothermal process and heat-treatment. Firstly, a piece of nickel foam (NF) was ultrasonically cleaned in HCl, ethanol solution and deionized (DI) water for 10 min, separately. Subsequently, the NF was immersed in a 50 mL Teflon-lined autoclave with a solution consisting of 1 mmol  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , 1 mmol  $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ , 6 mmol  $\text{CO}(\text{NH}_2)_2$ , and DI water. After that, the autoclave was held for eight hours at  $120^\circ\text{C}$ . The precursor was repeatedly cleaned using ethanol and water in turn, and it was then vacuum-dried for 12 h at  $60^\circ\text{C}$ . Lastly, the precursor was annealed for 2 h at  $300^\circ\text{C}$  in Ar to obtain  $\text{Fe}_2\text{O}_3/\text{SnO}_2/\text{NF}$ , followed by calcination for 2 h in a  $\text{H}_2/\text{Ar}$  (10:90) atmosphere. The catalyst obtained was named  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ . The pristine  $\text{Fe}_3\text{O}_4/\text{NF}$  catalyst was fabricated by the same method without adding  $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ . The synthesis of  $\text{SnO}_2/\text{NF}$  catalyst was described in the [Supplemental materials](#).

### 2.2. Characterizations

The morphology of samples was characterized by scanning electron microscopy (SEM, FlexSEM 1000), high-resolution transmission electron microscopy (HRTEM), and transmission electron microscopy (TEM, FEI Tecnai F20). X-ray diffraction (XRD) was carried out on a Bruker D2 PHASER system using  $\text{Cu K}\alpha$  radiation.  $^1\text{H}$  NMR spectra were acquired by a Bruker AV600 spectrometer (Switzerland). Chemical state information was obtained by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha spectrometer. The ultraviolet-visible (UV-vis) absorbance was obtained on TU-1901 (Beijing General Analysis Instrument Co., Ltd.). The X-ray absorption fine structure spectra (Fe K-edge) were collected at 1W1B station in Beijing Synchrotron

Radiation Facility (BSRF). The in situ Raman spectra were obtained by an inVia laser micro Raman spectrometer (Renishaw, UK).

### 2.3. Electrochemical measurements

Benefiting from the abundant heterointerfaces,  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  was employed as electrocatalysts for NRA. Electrochemical measurements were carried out on a CHI 660E electrochemical workstation with an H-type electrolytic cell at ambient condition. The cathode and anode chambers of the electrolytic cell were separated by a Nafion 211 membrane. The prepared  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  electrocatalyst, Pt wire, and Ag/AgCl electrode were assembled into a three-electrode system for the electrocatalytic study. The anode electrolyte was 0.5 M  $\text{K}_2\text{SO}_4$  solution (20 mL), while the cathode was 0.5 M  $\text{K}_2\text{SO}_4$  + 200 ppm  $\text{KNO}_3\text{-N}$  solution (20 mL). The linear sweep voltammetry (LSV) curves were recorded at a scan rate of  $5 \text{ mV s}^{-1}$ . Furthermore, the chronoamperometric measurements (*i-t*) were performed at different potentials for 1 h under a stirring speed of 500 rpm. Potential versus RHE was calculated using the formula  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH}$ . Electrochemical impedance spectroscopy (EIS) was recorded with a frequency range from 10 kHz to 0.01 Hz and an amplitude of 5 mV at  $-0.49 \text{ V}$ . The electrochemically active surface area (ECSA) was estimated by measuring the double-layer capacitance ( $C_{\text{dl}}$ ) via the CV test at scan rates of  $6\text{--}16 \text{ mV s}^{-1}$ . The detailed analytical methods for the determination of products NRA are supplied in the [Supporting Information](#).

### 2.4. Calculation details

First-principles calculations were performed based on the density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP) [33]. The projector-augmented wave (PAW) approach [34] with a cutoff energy of 520 eV, and dispersion corrections were calculated using the DFT-D3 method of Grimme [35]. To account for the strong on-site Coulombic interactions from the localization of the Fe 3d orbitals, an effective U value of 5.3 eV was applied using the DFT+U method by Dudarev et al. [36]. The  $\text{Fe}_3\text{O}_4$  (220) and  $\text{SnO}_2$  (110) surfaces were selected as the model for theoretical calculations. The vacuum layer in the z-axis direction was set at  $15 \text{ \AA}$ . The Brillouin zone was sampled by  $2 \times 2 \times 1$  special k-points [37]. The force convergence thresholds were  $0.02 \text{ eV}\cdot\text{\AA}^{-1}$  and the total energy less than  $10^{-5} \text{ eV}$ , respectively. The associated free energy is determined from Eq. (1):

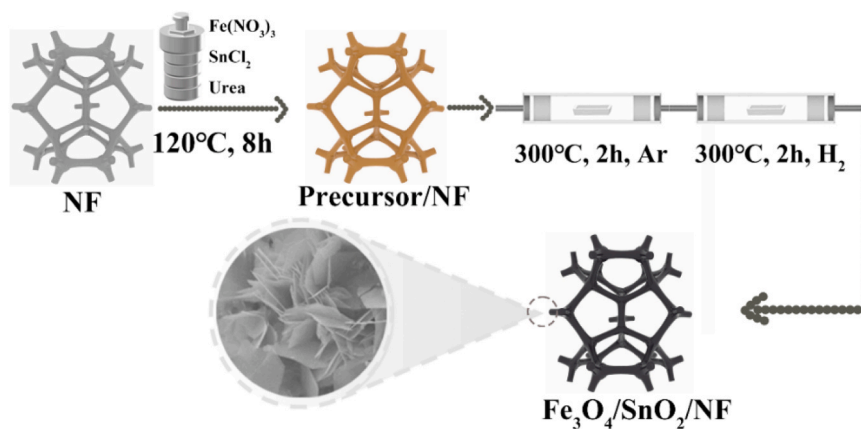
$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S \quad (1)$$

where  $\Delta E$  is the total energy change before and after intermediate adsorbed,  $\Delta E_{\text{ZPE}}$  is the change of zero-point energy, and  $\Delta S$  is the entropy change between the adsorbed state and gas phase. The energy of charged  $\text{NO}_3^-$  is not calculated directly; instead, gaseous  $\text{HNO}_3$  is used as a reference [38–40].

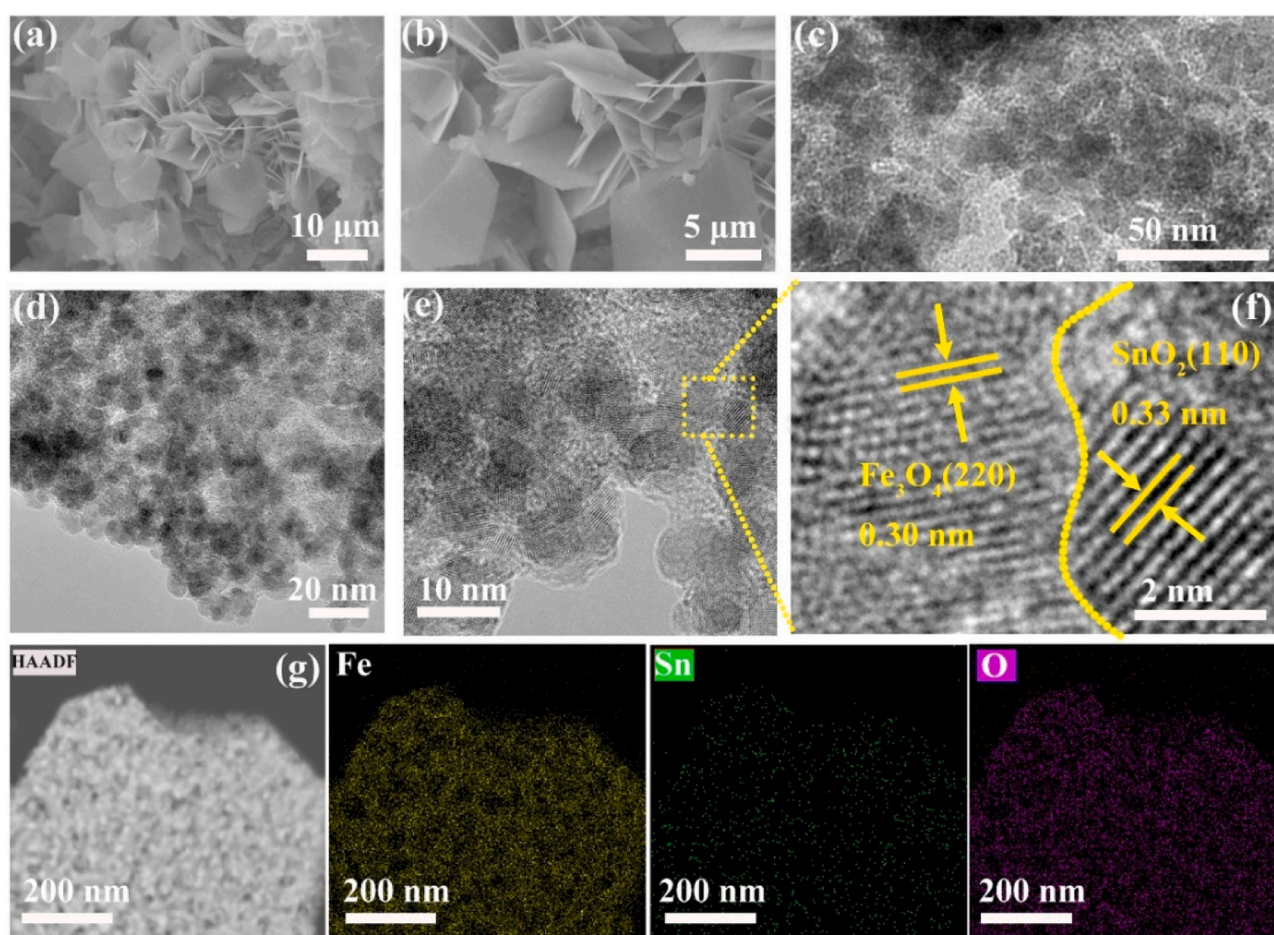
## 3. Results and discussion

### 3.1. Characterization of catalysts

$\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  was fabricated using a combination of hydrothermal process and heat-treatment (Scheme 1). SEM and TEM were used to investigate micromorphology of the samples. The SEM images of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  (Fig. 1a and b) clearly show that the 2D nanosheets are completely grown on the NF. The morphology of the control samples  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$  are shown in Figs. S1 and S2. The TEM images further confirm the nanosheet morphology of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  (Fig. 1c and d), and clearly demonstrates the heterointerfaces of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  (Fig. 1e). Furthermore, the magnified TEM image of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  (Fig. 1f) exposes the lattice fringe distances of 0.30 nm and 0.33 nm, indexed to the (220) and (110) planes of  $\text{Fe}_3\text{O}_4$  and  $\text{SnO}_2$ , respectively, certifying again the successful formation of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  with



**Scheme 1.** A simplified illustration of the entire preparation procedure for the  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ .



**Fig. 1.** (a, b) Scanning electron microscope at different magnifications and (c, d) HRTEM images of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ . (e) TEM image of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  heterointerfaces. (f) Magnified TEM image of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  heterointerfaces. (g) TEM-EDX elemental mapping for Fe, Sn, and O.

heterointerfaces. Energy dispersive X-ray (EDX) mapping images (Fig. 1 g) show that Fe, Sn, and O disperse uniformly in the  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  catalyst.

During the synthesis, the samples were obtained after two steps of calcination. The sample obtained after the first calcination step was  $\text{Fe}_2\text{O}_3/\text{SnO}_2/\text{NF}$  (Fig. S3a). Then, using the  $\text{H}_2/\text{Ar}$  atmosphere to reduce  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , and the EPR experiments show that this process produces almost no oxygen vacancies on the catalyst surface (Fig. S3b). The crystal structure of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  was investigated by XRD. As shown in Fig. 2a, the XRD diffraction peaks are well ascribed to cubic  $\text{Fe}_3\text{O}_4$

(PDF#89-4319) and tetragonal  $\text{SnO}_2$  (PDF#41-1445). Moreover, the weak peaks located at  $44.5^\circ$ ,  $51.8^\circ$  and  $76.3^\circ$  were attributed to (111), (200), and (220) planes of NF substrate (PDF#04-0850). The  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$  were also synthesized successfully as the control samples (Fig. S4). As seen in Fig. 2b-d, XPS was used to examine elemental composition and surface chemical states of these materials. The survey spectra (Fig. 2b) of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  identify the presence of Ni, Fe, Sn and O. As shown in the XPS spectrum of Fe 2p in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  (Fig. 2c), the binding energies (BEs) at 711.57 and 724.98 eV can be ascribed to  $\text{Fe}^{2+}$ , and the other peaks at 714.90 and 729.59 eV are



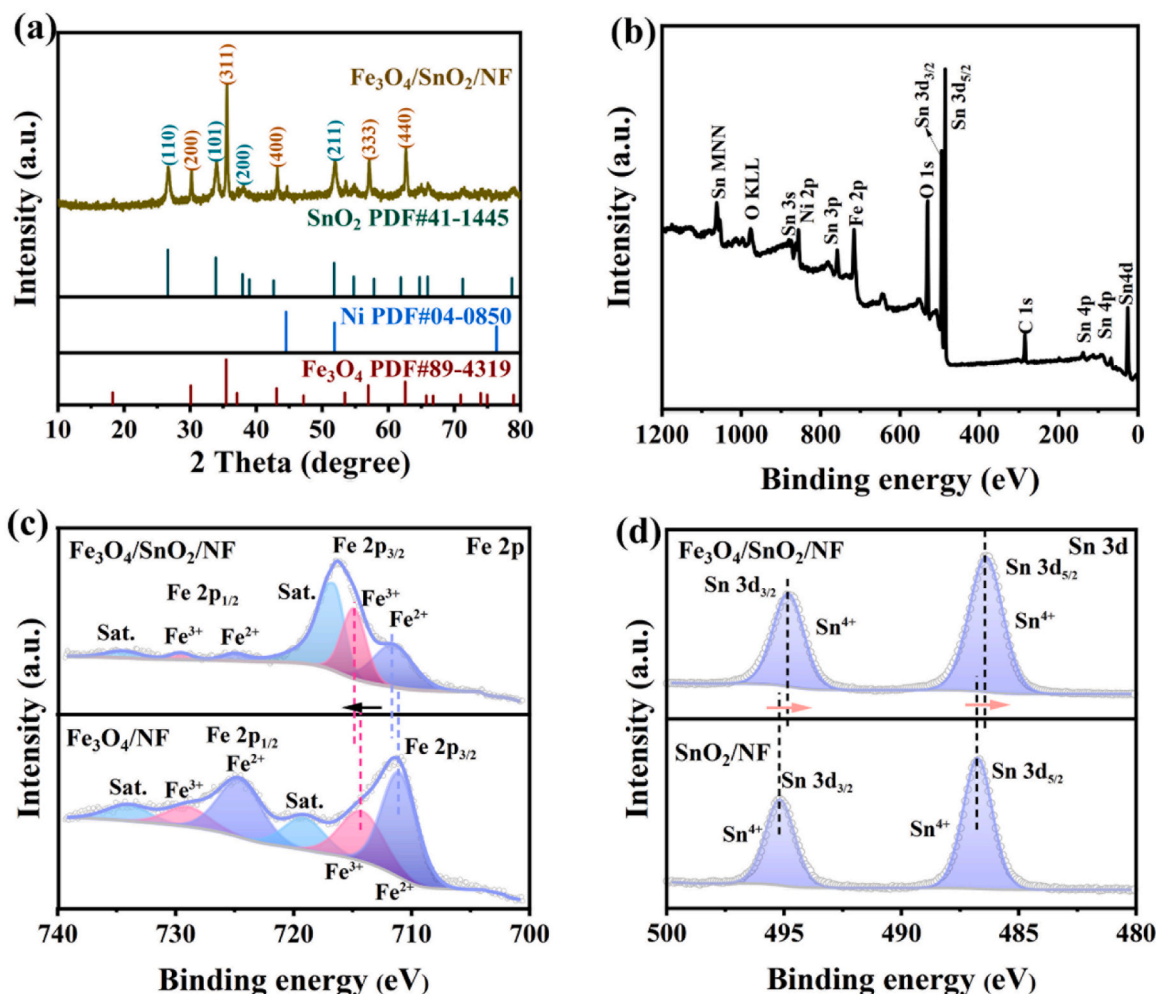


Fig. 2. (a) XRD pattern of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ . (b) XPS survey spectra of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ . (c, d) XPS spectra of Fe 2p and Sn 3d for  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ .

attributed to  $\text{Fe}^{3+}$ . The BEs located at 716.62 and 734.56 eV are assigned to the satellite peaks (Sat.) [41,42]. The Sn 3d spectrum of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  can be fitted into two peaks at 486.39 and 494.82 eV, belonging to  $\text{Sn } 3d_{5/2}$  and  $\text{Sn } 3d_{3/2}$ , respectively [42–44], which suggests that the Sn in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is  $\text{Sn}^{4+}$ . As compared to  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$ , the XPS peaks of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  positively shift by 0.52 eV and 0.65 eV, respectively, while that of  $\text{Sn}^{4+}$  in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  negatively shifts by 0.36 eV. The phenomenon can be explained by the different Fermi levels of  $\text{Fe}_3\text{O}_4$  and  $\text{SnO}_2$ , resulting in the charge transfer from  $\text{Fe}_3\text{O}_4$  to  $\text{SnO}_2$  [45], which suggests that the formation of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  with heterointerfaces can modulate the electronic structure of  $\text{Fe}_3\text{O}_4$  and  $\text{SnO}_2$ , thereby modulating the adsorption behavior of reaction intermediates.

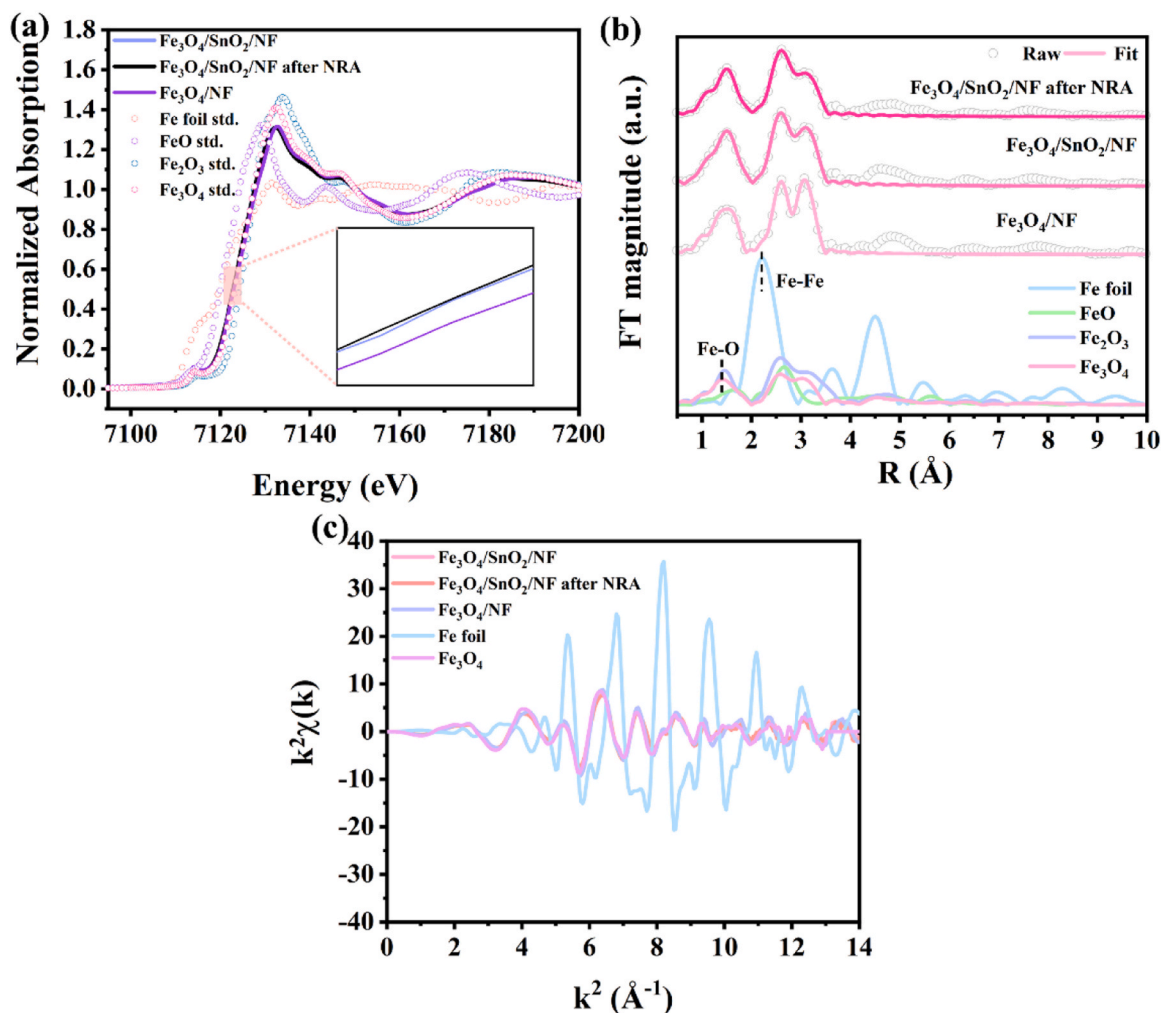
To further ascertain the fine structure of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  and the chemical state of Fe, the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were performed. Fig. 3a displays the Fe K-edge XANES of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , and Fe foil standard substances. The absorption edge of Fe K-edge in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is between  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , suggesting the oxidation state of Fe in the heterostructure is in the oxidation state between +2 and +3. Interestingly, the Fe K-edge absorption energy of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  after NRA is slightly negatively shifted compared with that of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  before NRA, which implies a slight decrease in the oxidation state of Fe. This result suggests that Fe species play a crucial role in the NRA process and may be the active site of NRA. The relevant Fe K-edge signal in  $k^3$ -weighted EXAFS spectra was recovered in order to define the local coordination environment, particularly the Fe

local structure. As shown in Fig. 3b, the EXAFS spectrum shows that the distance of Fe–O for  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is 1.50 Å, while Fe–O for  $\text{Fe}_3\text{O}_4/\text{NF}$  is 1.53 Å (Table S1). The fact that the bond distance of Fe–O is obviously shortened implies the Fe–O bond is stronger, further proving the significant electronic interaction between  $\text{Fe}_3\text{O}_4$  and  $\text{SnO}_2$  [46,47]. As shown in Fig. 3b, the EXAFS spectrum shows the presence of Fe–O bonds in the initial  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ . After NRA, the Fe–O bonds still exist in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ . Furthermore, the Fe K-edge EXAFS  $k^3\chi(k)$  oscillation curve of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  exhibits a similar frequency before and after the NRA testing (Fig. 3c). The result indicates that the catalyst still remains the structure of metal oxide and demonstrates the good stability of the catalyst.

### 3.2. Electrochemical performance

The electrocatalytic performance of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  was measured to evaluate the NRA catalytic activity. The linear scanning voltammetry curve (LSV) of catalysts were determined in 0.5 M  $\text{K}_2\text{SO}_4$  + 200 ppm  $\text{KNO}_3$  and blank electrolyte. It is worth noting that the current density of the  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  in the nitrate can reach  $114 \text{ mA cm}^{-2}$  (Fig. 4a, orange line) is much higher than that in the blank electrolyte at the same potential ( $78 \text{ mA cm}^{-2}$ , purple line), verifying that  $\text{NO}_3^-$  participates in the reduction reaction. The  $i$ -t tests were carried out from  $-0.29$  to  $-0.69 \text{ V}$  (Fig. S5). The absorbance of the diluted electrolyte was detected by UV–visible (UV–Vis) spectrophotometry (Fig. S6). The ammonia yield and FE were further calculated from the standard curve (Figs. S7–9). With continuously decreasing application potential, the





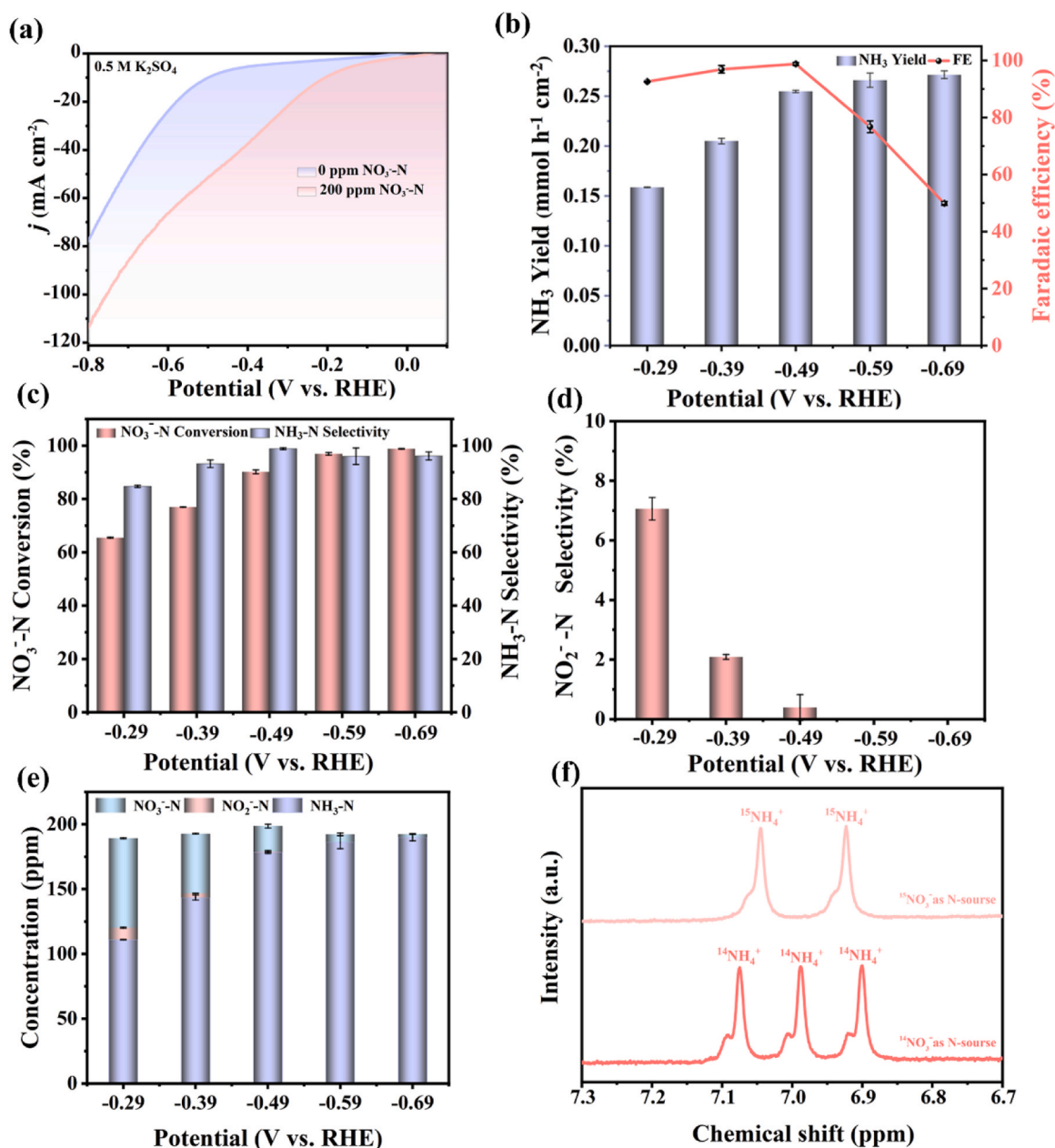
**Fig. 3.** (a) XANES spectra of the Fe K-edge (the inset is the enlarged absorption edge). (b) The  $k^3$ -weighted Fourier-transformed EXAFS R-space patterns. (c) Oscillation plots of EXAFS.

ammonia yield and  $\text{NO}_3^-$  conversion are gradually increasing. However, FE shows a volcanic trend (Fig. 4b and c) due to the gradual enhancement of the competitive HER. At  $-0.49$  V, FE, ammonia yield, ammonia selectivity, and  $\text{NO}_3^-$  conversion of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  reached 98.78%, 0.2548  $\text{mmol h}^{-1} \text{cm}^{-2}$ , 98.85%, and 90.19%, respectively. The NRA performance of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is superior to most of the catalysts reported so far (Table S3). The  $\text{NO}_2^-$  selectivity shows a clear downhill trend at more negative potential, which only reached 0.3896% at  $-0.49$  V, much smaller than ammonia selectivity (98.85%, Fig. 4d). Fig. 4e reveals that the  $\text{NO}_2^-$  is detected only in the lower potential range ( $-0.29 \sim -0.49$  V). Besides, during the time-dependent NRA electrolysis (Fig. S10),  $\text{NO}_3^-$ -N concentration drops dramatically while  $\text{NH}_3$ -N concentration increases significantly. The concentration of  $\text{NO}_2^-$  shows a volcano trend, suggesting that the  $\text{NO}_3^-$  is firstly reduced to  $\text{NO}_2^-$  and then progressively hydrogenated to  $\text{NH}_3$  during the NRA process.

The ammonia yields of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  were tested in the electrolyte containing 200 ppm  $\text{KNO}_3$ -N and no  $\text{KNO}_3$ . In addition, the ammonia yields of the pure NF and the open circuit potential (OCP) were tested. Ammonia yields are negligible in the blank electrolyte, the OCP conditions, and the pure NF (Fig. S11). This result proves that the ammonia production originates from the electrochemical  $\text{NO}_3^-$  reduction. Isotope labeling experiments were conducted to further examine the origin of ammonia production, employing  $^{15}\text{NO}_3^-$  and  $^{14}\text{NO}_3^-$  as the additive electrolyte. The  $^1\text{H}$ NMR spectrum of  $^{15}\text{NH}_4^+$  shows double peaks, while  $^{14}\text{NH}_4^+$  shows triple peaks, which suggests that ammonia is exclusively

derived from  $\text{NO}_3^-$  reduction (Fig. 4f) [48]. In order to comprehensively evaluate the NRA performance for  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ , the contrastive catalysts including  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$  were measured. Notably, the current density of  $\text{Fe}_3\text{O}_4/\text{NF}$ ,  $\text{SnO}_2/\text{NF}$ , and  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is obviously different (Fig. 5a). Compared to other contrastive catalysts,  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  exhibits more positive onset potential and higher current density, suggesting that  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  has more excellent electrocatalytic activity for nitrate reduction. As shown in Fig. 5b and c, the FE (98.78%),  $\text{NH}_3$  yield (0.2548  $\text{mmol h}^{-1} \text{cm}^{-2}$ ), and  $\text{NO}_3^-$  conversion (90.19%) of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  at  $-0.49$  V are much higher than those of  $\text{Fe}_3\text{O}_4/\text{NF}$  (77.61%, 0.0806  $\text{mmol h}^{-1} \text{cm}^{-2}$  and 40.64%, Fig. S12) and  $\text{SnO}_2/\text{NF}$  (45.60%, 0.0142  $\text{mmol h}^{-1} \text{cm}^{-2}$  and 14.10%, Fig. S13). Moreover, the  $\text{NO}_2^-$  selectivity of  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$  respectively reaches 11.50% and 13.05% at  $-0.49$  V, which is more than 30 times greater than that of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  (Fig. 5d). These results indicate that the formation of the heterointerfaces inhibits the generation of byproducts ( $\text{NO}_2^-$ ) and favors the production of  $\text{NH}_3$ . Namely, the construction of heterointerfaces is a promising strategy to improve the NRA performance.

In order to reveal the origin of the excellent catalytic performance of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$ , the ECSA of the catalyst was evaluated by  $C_{dl}$  tests (Figs. S14–16). The  $C_{dl}$  of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is significantly higher than that of  $\text{Fe}_3\text{O}_4/\text{NF}$  and  $\text{SnO}_2/\text{NF}$ , indicating that  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  owns larger active area and could expose more redox active sites. In addition, the EIS tests show that the charge transfer resistance of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$



**Fig. 4.** (a) LSV curves of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF tested in 0.5 M K<sub>2</sub>SO<sub>4</sub> + 200 ppm KNO<sub>3</sub> and blank electrolyte. (b) NH<sub>3</sub> yield and NH<sub>3</sub>-FE, (c) NO<sub>3</sub><sup>-</sup> conversion and NH<sub>3</sub>-N selectivity, (d) NO<sub>2</sub><sup>-</sup> selectivity of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF, (e) Concentration of different products after NRA electrolysis at various potentials. (f) <sup>1</sup>H NMR measurements fed by <sup>14</sup>NO<sub>3</sub><sup>-</sup>/<sup>15</sup>NO<sub>3</sub><sup>-</sup> after NRA.

is lower than that of Fe<sub>3</sub>O<sub>4</sub>/NF and SnO<sub>2</sub>/NF, demonstrating that Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF possesses better electron transport capability and thus favors the production of ammonia from a kinetic point of view (Fig. S17). To demonstrate that the Fe sites in Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF are active sites of NRA, the poisoning experiment was carried out using a stronger Lewis base, potassium thiocyanide (KSCN) [49,50]. As shown in Figs. 6a and 6b, after adding SCN<sup>-</sup> ions into the K<sub>2</sub>SO<sub>4</sub> solution containing NO<sub>3</sub><sup>-</sup>, the current density of NRA decreases significantly due to the poisoning of the Fe sites by SCN<sup>-</sup>. Correspondingly, the NH<sub>3</sub> yield also drops dramatically, while the current density of HER remains almost unchanged. This is due to the fact that the Fermi energy levels of Fe<sub>3</sub>O<sub>4</sub> and SnO<sub>2</sub> are significantly different, the self-driven electron donation from Fe<sub>3</sub>O<sub>4</sub> to SnO<sub>2</sub> can induce local charge redistribution around the Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub> heterointerfaces and endows the surface of Fe<sub>3</sub>O<sub>4</sub> with an electrophilic region, while the surface of SnO<sub>2</sub> is nucleophilic [45]. As a result, the positively charged Fe<sub>3</sub>O<sub>4</sub> surface is more favorable for

adsorption of electron-rich NO<sub>3</sub><sup>-</sup>, while the negatively charged SnO<sub>2</sub> surface is more favorable for adsorption of \*H. Thus, the Fe sites are poisoned due to preferentially occupied by the stronger Lewis base SCN<sup>-</sup> in the presence of SCN<sup>-</sup>, whereas the Sn sites are hardly poisoned and adsorbs \*H, which leads to a sharp decrease in the current density of NRA and the NH<sub>3</sub> yield, while the current density of HER remains almost unchanged. Obviously, the synergy of Fe sites and Sn sites boosts the efficiency of NRA.

To evaluate the NRA catalytic stability of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF, the successive cycling test was performed at -0.49 V. No significant decrease in ammonia yield, FE, selectivity and NO<sub>3</sub><sup>-</sup> conversion are observed after 11 cycles (Figs. 6c, 6d and S18). Meanwhile, the nanosheet structure of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF shows no apparent changes after the cyclic stability tests, and the phase remains unchanged (Fig. S19). The above results suggest that Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF has admirable catalytic stability and structural stability for NRA. As shown in Figs. S20a and 20b, the NRA

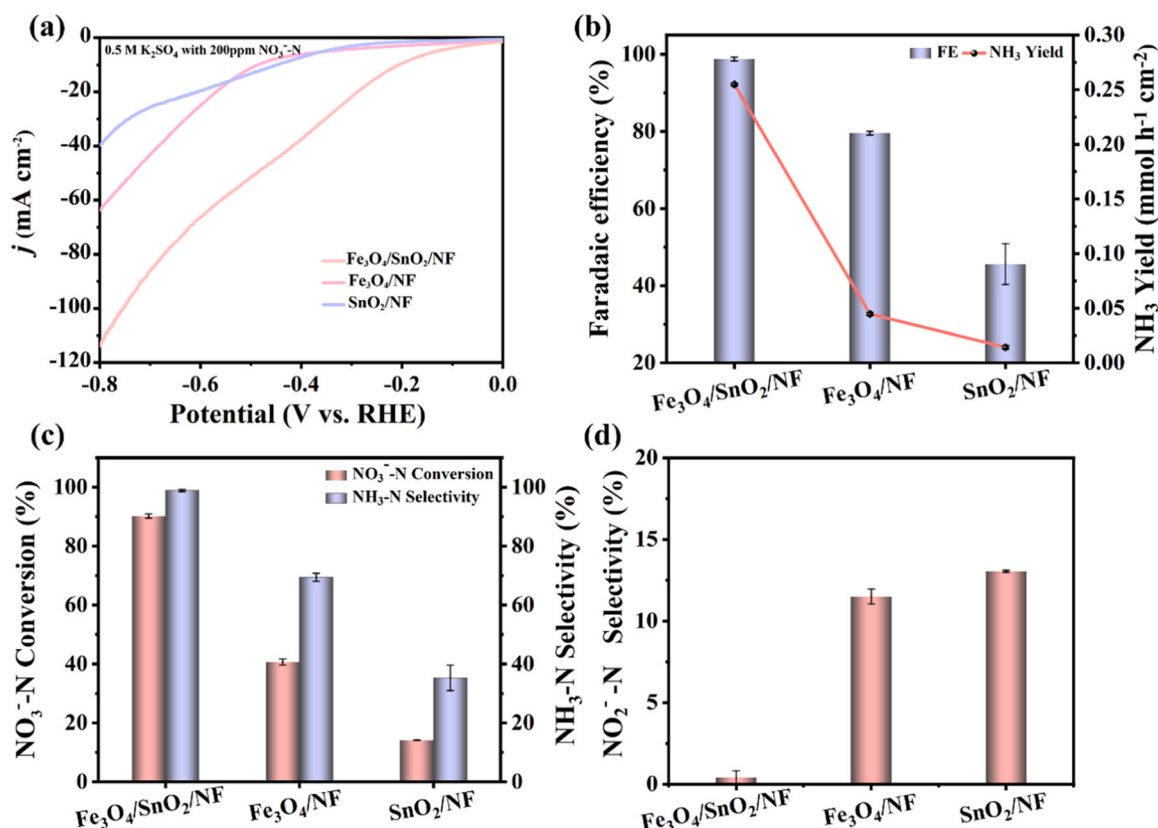


Fig. 5. (a) LSV curves, (b) Faradaic efficiency and  $\text{NH}_3$  yield rates, (c)  $\text{NO}_3^-$  conversion and  $\text{NH}_3$ -N selectivity, (d)  $\text{NO}_2^-$ -N selectivity of three samples.

tests were conducted for 1 and 2 h at nitrate concentrations of 500 ppm, 1000 ppm, and 1400 ppm, respectively. The results showed that the NRA performance of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  was not satisfactory and was not as good as that at nitrate concentrations of 200 ppm. To investigate the effect of impurities on catalyst performance, the NRA performance testing of the as-prepared catalyst in the presence of other coexisting ions were performed (Figs. S20c and S20d). In the presence of impurities (including  $\text{CO}_3^{2-}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{HCO}_3^-$ ,  $\text{Li}^+$ , and their concentration is 200 ppm), the NRA performance and selectivity of the catalyst remain excellent, indicating its potential for application.

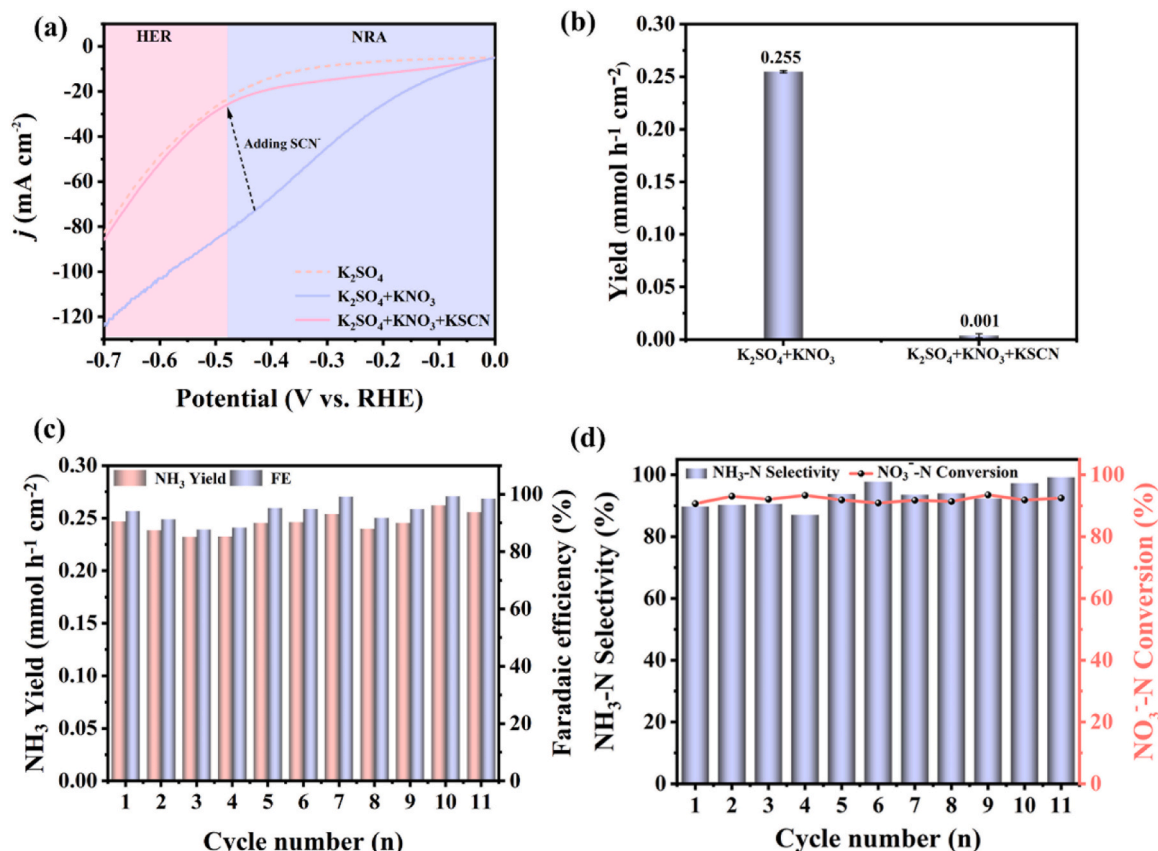
### 3.3. Mechanism investigation

To further reveal the high activity origin of the  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  catalyst, the DFT calculations were performed. Based on the TEM characterization results (Fig. 1 f), the (220) of  $\text{Fe}_3\text{O}_4$  and (110) of  $\text{SnO}_2$  planes were selected as the calculated models (Figs. S21 and S22). The project density of states (PDOS) in Fig. 7a shows that the level of the d-band center of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is closer to the Fermi energy level compared to  $\text{Fe}_3\text{O}_4/\text{NF}$ , indicating that the formation of heterointerfaces in  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  enhances the absorption of nitrate and NRA intermediates. Due to the need for protons in NRA, the moderate HER activity of the catalyst is beneficial to NRA (water in the electrolyte serves as the proton source). Therefore, the adsorption energy, dissociation energy, and  $\text{H}_2$  generation energy of water molecules at the Fe and Sn sites were calculated separately, and the results are shown in Figs. 7b and S23. Apparently, these energies at the Fe sites are much higher than those at the Sn sites [3,18], indicating that the Sn sites are more favorable to HER, and thus Sn rather than Fe is the active site of HER. From an energy perspective, the Fe sites with NRA activity are not conducive to HER. These findings reveal that Fe on  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  is the primary active site facilitating the adsorption and activation of  $\text{NO}_3^-$  and inhibiting the HER side reaction, while Sn is the active site of HER to

provide  $^*\text{H}$ . In a word, this synergistic effect of Fe and Sn sites contributes to the excellent NRA activity and selectivity of  $\text{Fe}_3\text{O}_4/\text{SnO}_2/\text{NF}$  with heterointerfaces.

The intermediates of the reaction process were monitored by in situ Raman. As shown in Fig. S24, the peak strength of 982 cm<sup>-1</sup> corresponds to  $\text{SO}_4^{2-}$  from the electrolyte. Several peaks at 1011, 1186, and 1450 cm<sup>-1</sup> are observed, which can be assigned to the  $\text{NO}_3^-$  stretching vibration of adsorbed  $\text{NO}_3^-$ , the stretching vibration of  $\text{NO}_2^-$ , and the stretching vibration of N = O, respectively.[51] The two signals located at 1140 and 1516 cm<sup>-1</sup> respectively come from the  $\text{NH}_2$  wagging and NH bending, whose intensities increase over potential.[52] The peak near 1584 cm<sup>-1</sup> is the HNH bending vibration of  $\text{NH}_3$  and its intensity is weak, indicating that the generated  $\text{NH}_3$  can quickly desorb from the catalyst surface, which is beneficial for NRA.[53,54] Based on the above findings, a potential NRA mechanism is proposed. First,  $\text{NO}_3^-$  is adsorbed on the catalyst surface and reduced to the intermediate product  $^*\text{NO}_2$  ( $^*$  denotes the state of being adsorbed) [22,28]. Then,  $^*\text{NO}_2$  undergoes a deoxidation reaction to form  $^*\text{NO}$ . Through gradual hydrogenation,  $^*\text{NO}$  may form  $^*\text{NOH}$  (Pathway 1) and  $^*\text{NHO}$  (Pathway 2). The  $^*\text{NOH}$  and  $^*\text{NHO}$  intermediates undergo a stepwise hydrogenation reaction (Pathway 1:  $^*\text{NOH} \rightarrow ^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3 \rightarrow \text{NH}_3$ , Pathway 2:  $^*\text{NHO} \rightarrow ^*\text{NHOH} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3 \rightarrow \text{NH}_3$ ) to generate  $\text{NH}_3$ . Thus,  $^*\text{H}$  produced by  $\text{H}_2\text{O}$  dissociation embodies a critical role in NRA. The Gibbs free energy changes ( $\Delta G$ ) of NRA pathways on  $\text{Fe}_3\text{O}_4/\text{SnO}_2$  were calculated. The intermediates associated with Pathway 1 and Pathway 2 of NRA were calculated on  $\text{Fe}_3\text{O}_4/\text{SnO}_2$ , and the related structures of the NRA intermediates are shown in Fig. 7c (inset). In Pathway 1, a high  $\Delta G$  of 1.32 eV is obtained for the rate-determining step (RDS) from  $^*\text{NO}$  to  $^*\text{NOH}$ . From a thermodynamic perspective, Pathway 2 is more favorable on  $\text{Fe}_3\text{O}_4/\text{SnO}_2$ . As depicted in Figs. S25 and S26, for the steps  $^* + \text{NO}_3^- \rightarrow ^*\text{NO}_3$  on  $\text{Fe}_3\text{O}_4$  and  $^*\text{NH}_3 \rightarrow \text{NH}_3$  on  $\text{SnO}_2$ , the calculated  $\Delta G$  are respectively 1.58 and 3.43 eV, while that of these two steps on  $\text{Fe}_3\text{O}_4/\text{SnO}_2$  are only 0.66 and 0.86 eV. These results





**Fig. 6.** (a) LSV curves for poisoning experiment on Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF. (b) NH<sub>3</sub> Yield with SCN<sup>-</sup> and without SCN<sup>-</sup>. (c) Faradaic efficiency and NH<sub>3</sub> yield, (d) NH<sub>3</sub>-N selectivity and NO<sub>3</sub><sup>-</sup>-N conversion for 11 consecutive cycles.

indicate that Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub> possesses moderate \*NO<sub>3</sub> adsorption strength and \*NH<sub>3</sub> desorption strength. Therefore, Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF catalysts with heterointerfaces are more beneficial for NRA.

In addition, the electrostatic potential of SnO<sub>2</sub> (110) and Fe<sub>3</sub>O<sub>4</sub> (220) in the  $z$  direction was calculated. The static potential can be used not only as a work function ( $\Phi = E_{\text{vac}} - E_{\text{F}}$ ), but also as a powerful tool to analyze the surface electronic structure, such as the electron flow in the heterojunction model [55]. As shown in Fig. S27, the work functions of SnO<sub>2</sub> (110) surface ( $\Phi_{\text{SnO}_2} = 7.07$  eV) and Fe<sub>3</sub>O<sub>4</sub> (220) surface ( $\Phi_{\text{Fe}_3\text{O}_4} = 5.55$  eV) are compared, and the Fermi energy of SnO<sub>2</sub> is found to be lower than that of Fe<sub>3</sub>O<sub>4</sub> surface. Thus, in the Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub> heterointerfaces, electron will transfer from Fe<sub>3</sub>O<sub>4</sub> to SnO<sub>2</sub> until the two Fermi energies reach the same level (-1.77 eV) [45,56,57], which is consistent with the XPS results.

On the basis of all the above results, a synergistic catalysis mechanism of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF for NRA is concluded. The Sn sites encourage the dissociation of water and enhance the coverage of \*H on Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF, while the Fe sites adsorb and activate nitrate throughout the NRA electrochemical reaction. The produced \*H from Sn sites is provided to Fe sites, thus accelerates the hydrogenation reaction of intermediates and enhances the NRA activity of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF. In addition, Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF optimizes the adsorption of reaction intermediates, prevents the generation of byproducts NO<sub>2</sub><sup>-</sup> and inhibits the occurrence of HER.

#### 4. Conclusions

In conclusion, Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF with heterointerfaces was designed and constructed for NRA. The electronic interaction at heterointerfaces induces charge redistribution, thus improving the performance of NRA. Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF showed excellent performance at -0.49 V. (NH<sub>3</sub>

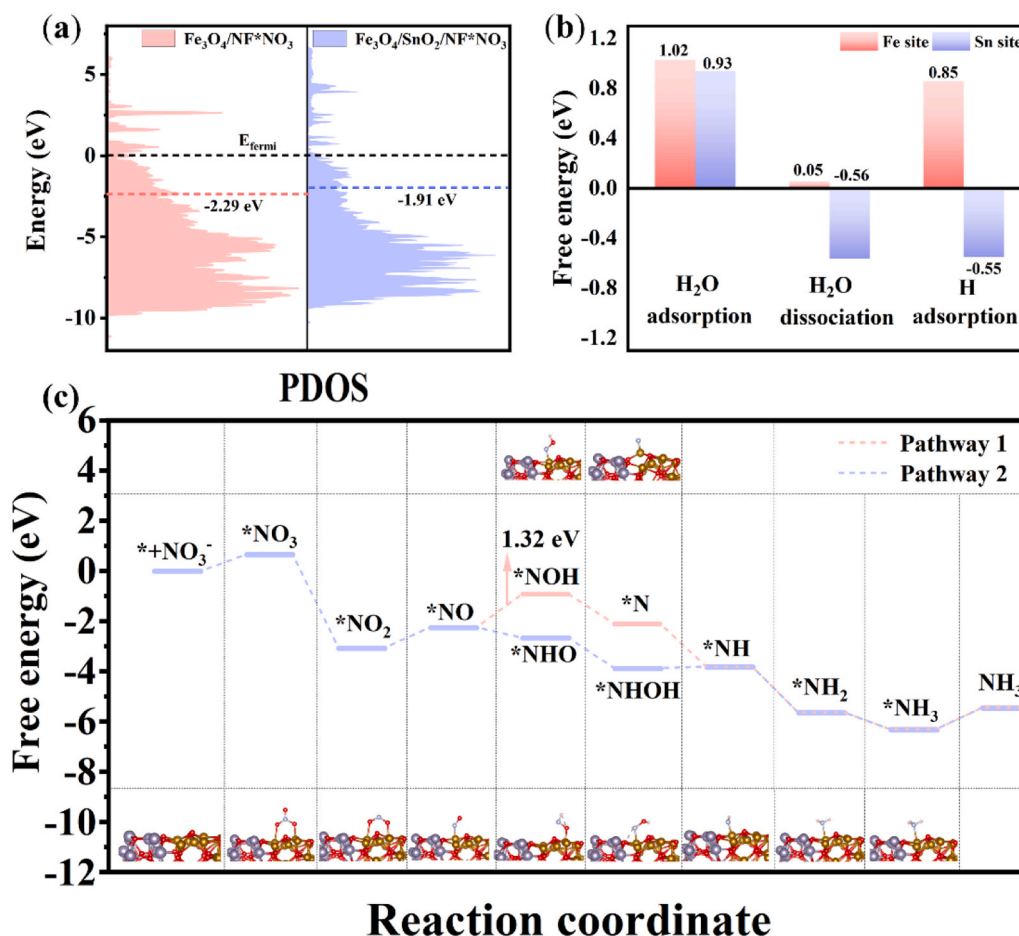
Faradaic efficiency: 98.78%, NH<sub>3</sub> yield: 0.2584 mmol h<sup>-1</sup> cm<sup>-2</sup>, NH<sub>3</sub> selectivity: 98.85%, and NO<sub>3</sub><sup>-</sup> conversion: 90.19%), which is significantly better than Fe<sub>3</sub>O<sub>4</sub>/NF and SnO<sub>2</sub>/NF. Combining experimental and theoretical calculations, the synergistic catalytic mechanism of Fe<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>/NF was revealed, in which the Fe sites activate nitrate while the Sn sites accelerate H<sub>2</sub>O dissociation and provide sufficient \*H to facilitate further hydrogenation process. This work reveals the essence of heterointerface engineering to activate nitrate, optimize the adsorption of NRA intermediates, and inhibit the occurrence of side reactions, which has guiding significance for the design and preparation of highly efficient NRA catalysts.

#### CRediT authorship contribution statement

**Gou Qiao:** Writing – original draft, Validation, Methodology, Investigation, Data curation. **He Rongxing:** Writing – review & editing, Resources, Funding acquisition, Formal analysis. **Wang Yun:** Software, Resources, Investigation. **Li Ming:** Methodology, Conceptualization. **Shen Wei:** Software, Resources, Investigation. **Jiang Yimin:** Resources, Investigation. **Gou Fenglin:** Software, Resources, Investigation. **Lv Shengmei:** Software, Resources, Investigation. **Mao Yini:** Software, Resources, Investigation.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



**Fig. 7.** (a) Project density of states of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{SnO}_2$  after adsorption of  $*\text{NO}_3$ . (The dashed lines are the position of the d-band center). (b) HER pathways on Fe and Sn sites of  $\text{Fe}_3\text{O}_4/\text{SnO}_2$ . (c) Free energy changes of the NRA reaction for different intermediates of two pathways on  $\text{Fe}_3\text{O}_4/\text{SnO}_2$ .

## Data availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2024.123810](https://doi.org/10.1016/j.apcatb.2024.123810).

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